SPECTRUM OF DOUBLY-IONISED CADMIUM

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ABSTRACT. An experimental investigation of the spark spectrum of cadmium has been made, the range of spectrum extending from λ2200 to 370A. The lines corresponding to different stages of ionisation have been sorted out by introducing inductance in the spark circuit. 134 new lines of Cd III have been classified identifying 29 new terms which consist of $4d^9 6s$, $4d^9 5d$ and 7 undesignated terms. The term values have been calculated by means of the 5s-5p and 5p-6s groups of lines. The value obtained for the deepest term, $4d^{10}\ {}^1S_0$, is 308463 cm^{-1}; the corresponding ionisation potential is about 38 volts.

EXPERIMENTAL

The experimental part of this investigation was carried out at 'Upsala,' Sweden, in 1931-32 when the writer was working under the Late Prof. A. Fowler, F.R.S., in the Imperial College of Science and Technology, London, on the isoelectronic spectra of Cu, Zn, Ag, Cd, etc. Through the kindness of Prof. Siegbahn the spectra of the above elements were taken in the Physical Laboratory at Upsala with two 'grazing incidence' spectrographs. In one, the grating was of radius 1.5 metres and in the other, 1 metre. The source employed was the 'hot spark' excited by means of rectified and condensed current of tension of about 50 to 70 kilo-volts. The range of the spectra photographed was from λ2200 to 370A, the dispersion varying from 5.71A per mm. at 2200A to 2.80A per mm. at 400A. The definition was extremely good and the lines as close as 0.10A were clearly separated.

The lines belonging to the different stages of ionisation were distinguished from each other by inserting some suitable inductance in the spark circuit. By adjusting the amount of inductance and the time of exposure the lines of Cd III were obtained with approximately the same intensity with and without inductance. Cd IV lines were prominent without inductance and suppressed with inductance. The reverse was the case with the Cd II lines. The lines of which the intensities are equal with and without inductance or differ by '1' are taken to be the Cd III lines—the most prominent lines having been given the intensity '10.' The faint lines where this criterion cannot sometimes be applied have been treated as Cd III lines whenever they are found to fit into the analytical scheme.

CLASSIFICATION

The doubly-ionised cadmium is isoelectronic with singly ionised silver and neutral palladium and a general similarity of the three spectra, Cd III, Ag II

and Pd I is to be expected. In accordance with Hund's theory the triplet and singlet terms arising from the atoms in the unexcited and various excited states may conveniently be represented as in Table I which indicates the types of terms arising from the more important configuration shown on the left.

TABLE I

4s	4p	4d	4f	5s	5p	5d	5f	6s	6p	Prefix	Terms
2	6	10								$4d^{10}$	$^1S_0$
2	6	9		1						$4d^9 5s$	^1D, ^3D
2	6	9			1					$4d^9 5p$	$^1(PDF)$, $^3(PDF)$
2	6	9						1		$4d^9 6s$	^1D, ^3D
2	6	9				1				$4d^9 5d$	$^1(SPDFG)$, $^3(SPDFG)$
2	6	9							1	$4d^9 6p$	$^1(PDF)$, $^3(PDF)$
2	6	8		2						$4d^8 5s^2$	$^1(SDG)$, $^3(PF)$
2	6	8		1	1					$4d^8 5s 5p$	$^5(DFG)$, $^3(DFG)$, etc.

The lines corresponding with the possible combinations of the first three rows have already been measured and identified by Gibbs and White (1928), and independently by McLennan, McLay, and Crawford (1928). In the course of the present investigation all the terms shown in the fourth and the fifth row have been identified. The terms $^3F_4$, $^3F_3$, $^3F_2$ and $^3P_2$ belonging to the configuration $4d^8 5s^2$ and probably the terms $^5D_3$, $^3F_3$ belonging to the configuration $4d^8 5s 5p$ for Pd I have been identified by Shenstone, (1930). But none of the terms belonging to the above two configurations have been identified in the case of Ag II. The terms $3d^8 4s^2$ and $3d^8 4s 4p$ for Ni I (Russel 1929) have been found to give very bright lines in combination with the $3d^9 4p$ and $3d^9 4s$ terms respectively. No traces of these lines have, however, been found in the case of Cu II, though the spectrum was excited by the very powerful method of "hollow cathode" (Kruger, 1929).* But in the case of Zn III the terms $3d^8 4s$ (^4F) $4p^5$, $^3(DFG)$ and the terms $3d^8 4s$ (^2F) $4p^3$, $^1(DFG)$ have been identified by the present writer (Mazumder, 1936; Mazumder 1934-35). The terms $3d^8 4s^2$ $^1(SGD)$ $^3(PF)$ could not however, be located for Zn III. In the spectrum of Cd III a large number of lines giving the characteristic differences of the $4d^9 5s$ terms appeared just below λ600A. These lines do not combine into a Rydberg sequence of $4d^9 np$ terms with $4d^9 5p$ terms already known—the expected region for $4d^9(5s\text{-}6p)$ lines being in the neighbourhood of λ700A. Like Zn III these Cd III lines should then also be due to the combination of $4d^9 5s$ terms with

* Shenstone has, however, later identified the terms $3d^8 4s^2$ and $3d^8 4s 4p$ for Cu II; *Phil. Trans. Roy. Soc*, 235A, p. 195, March 12, 1936.

$4d^8 5s5p$ terms. In the absence of the corresponding data for Ag II and Pd I it is difficult to identify the terms $4d^8 5s5p$ for Cd III. The work is, however, being continued and this part will form the subject matter for a future communication.

A few lines are still available in the region where $4d^9(5p\text{-}6s)$ and $4d^9(5p\text{-}5d)$ lines appear. Some of these residual lines give characteristic differences of $4d^9 5p$ terms. They probably arise from the combination of $4d^9 5p$ terms with $4d^8 5s^2$ terms. But most of the minor combinations being absent, the lines concerned are here shown as due to the combinations of $4d^9 5p$ terms with a few undesignated terms. It should be remembered that the transition is a double electronic one and all the satellite and intercombination lines may not appear.

There can be no doubt that the strong group of lines λ2225 to 1470A has been correctly classified by Gibbs and White as arising from the combination of $4d^9 5s$ and $4d^9 5p$ terms. The lines occur in the region which is to be expected from a comparison with corresponding groups in the isoelectronic spectra Pd I and Ag II. By applying the irregular doublet law it is found thus:

		$5s\ ^3D_3$	—	$5p\ ^3D_3$
Pd I	... ...	30829		
				16464
Ag II	... ...	47293		
				15149
Cd III	... ...	62442		

where the $\Delta\nu$'s are in the usual order of agreement in such comparisons. Moreover, the terms of Ag II and Cd III are arranged in the same order of magnitude and the $\Delta\nu$'s in the components of triplets have generally the same sign.

The expected regions for (5p-6s) and (5p-5d) groups of lines are in the neighbourhood of the (5s-5p) group. On examining the lines just below the (5s-5p) group a large number of differences characteristic of the 5p terms have been obtained. It has been possible to arrange the lines as due to the possible combinations of 5p terms with the 6s and 5d terms. As mentioned earlier, by means of some of the residual lines a few terms have been obtained which, though left undesignated, are most probably the $4d^8 5s^2$ group of terms.

The 5s and 6s groups having been established, it has been possible to calculate the absolute term values by means of a simple Rydberg formula. The value for the $5s\ ^3D_3$ term is found to be 228000 cm^{-1}. This places the deepest term $4d^{10}\ ^1S_0$ at 308463 cm^{-1}; the corresponding ionization potential is about 38 volts.

Comparison of the three Isoelectronic Spectra, Pd I, Ag II and Cd III

It is of interest to compare the term values of isoelectronic spectra Pd I, Ag II and Cd III as in the following table:

The values of the $4d^9 6s$ (^{3,1}(D)) Terms

	$^3D_3$	$^3D_2$	$^3D_1$	$^1D_2$
Pd I	18476(216)	18260(3316)	14944(152)	14792
Ag II	56637(377)	56260(4215)	52045(279)	51766
Cd III	104033(488)	103545(5315)	98230(366)	97864

It will be seen that the separations of the terms have systematically increased with the nuclear charge.

Separation of the Triplet D Term

	$4d^9 5s$		$4d^9 6s$	
	(1, 2)	(2, 3)	(1, 2)	(2, 3)
Pd I	2339	1191	3316	216
Ag II	2998	1577	4215	377
Cd III	3866	1900	5315	488

The above figures show that the difference, $^3D_2 - {}^3D_1$, has increased with the quantum number, whereas $^3D_3 - {}^3D_2$ has decreased. The total separation has, however, remained practically the same. It is evident from this that the separation of the ground terms $4d^9\ ^2D_{3,2}$ of Cd IV will approximately be—

$$(3866 + 1900) + (5315 + 488)/2 \text{ or } 5785 \text{ cm}^{-1}.$$

The actual value found by Green (1941) is 5812; thus the agreement is very close.

Application of the Irregular Doublet Law

	$5s^3D_3$	$5p^3D_3$	$5s^3D_3 - 5p^3D_3$		$(5s^3D_3)^{\frac{1}{2}} - (5p^3D_3)^{\frac{1}{2}} = \Delta(\nu\frac{1}{2})$
PD I	60716	29887	30829		73.5
				16464	
Ag II	138000	90707	47293		70.3
				15147	
Cd III	228000	165560	62440		70.6

According to the irregular doublet law '$\Delta\nu\frac{1}{2}$' is independent of the nuclear charge which is found to be approximately the case from the figures given in the last column. It is interesting to point out that the corresponding figures for Ni I, Cu II, and Zn III given in the author's papers mentioned earlier are 69.1, 71.8 and 72.2 respectively.

In Fig. 1 the Moseley diagrams for terms $4d^{10}\ ^1S_0$ $4d^9 5s\ ^3D_3$, $5p^3D_3$ and $6s^3D_3$ for the three isoelectronic spectra Pd I, Ag II and Cd III are drawn. The figures for Cd III are based upon $5s^3D_3 = 228000$ cm^{-1} calculated from the data obtained in the present investigation. The curves corresponding to the terms $5s^3D_3$ and $5p^3D_3$ run fairly parallel. All the curves bend slightly downwards with increasing Z.

In Table II the wave numbers of the lines classified as due to the combination of 5p and 6s terms are given. For completeness the (5s-5p) group of lines given by Gibbs and White is also included. The figures just above the wave numbers indicate intensities. The term values written near the respective terms are those obtained by the author.

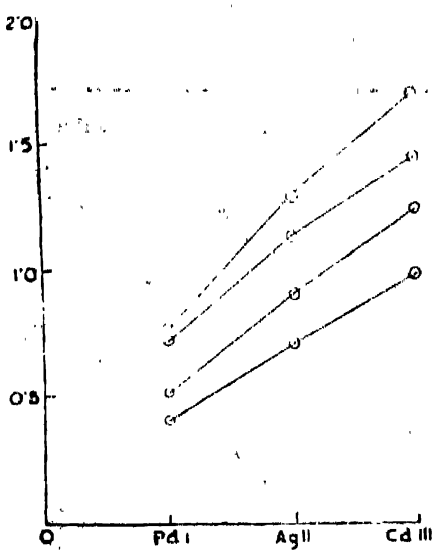

Fig. 1

Moseley diagram for Pd I, Ag II, Cd III

In Table III are given the designation of the terms and the corresponding values; in Table IV, the wave-length, wave numbers, intensities and classification. The lines against which the letters G. and W. have been written are those classified by Gibbs and White; but the wave-length, frequencies and intensities mentioned are those obtained in the present investigation except for a few lines at the end of the table where the original figures have been retained. Against some of the lines "Gr IV has been written; these have also been used by Green in his analysis of Cd IV lines. Some of these lines

TABLE II

$4d^9 5p$	$4d^{10}$ $^1S_0$ 308463	$^3D_3$ 228000	$1900\ ^3D_2$ 226100	$4d^9 5s$ $3866\ ^3D_1$ 222234	$2652\ ^1D_2$ 219582	$^3D_3$ 104033	$4d^9 6s$ $488\ ^3D_2$ 103545	$5315\ ^3D_1$ 98230	$366\ ^1D_2$ 97864
169422 $^3F_4$	—	15	—	—	—	4	—	—	—
−2818		58578				65390			
172240 $^3F_3$	—	12	15	—	8	3	5	—	*
6541		55760	53859		47341	68207	68696		
165699 $^3F_2$	—	1	10	10	9	1	4	4	3
139		62300	60399	56535	53883		62152	67407	67835
165560 $^3D_3$	—	12	8	—	9	4	4	—	2
−2464		62439	60537		54022	61527	62015		67696
168024 $^3D_2$	—	1	7	12	5	1	3	4	2
7197		59971	58075	54211	51557		64478	69793	70160
160827 $^3D_1$	8	—	7	10	4	—	1	4	*
−13814	147637		65270	61405	58753		57282	62594	
174641 $^3P_2$	—	15	3	1	4	5	5	1	2
4942		53359	51459	47592	44941	70609	71096		76782
169699 $^3P_1$	8	—	12	5	6	—	3	1	5
3358	138765		56400	52535	49882		66153	71474	71834
166341 $^3P_1$	—	—	—	8	—	—	—	3	—
3980				55891				68112	
162361 $^1F_3$	—	5	8	—	12	*	*	—	4
2372		65636	63734		57219				64497
159989 $^1D_2$	—	4	5	7	12	1	*	4	3
−2389		68009	66110	62241	59595	55960		51758	62126
162378 $^1P_1$	15		3	5	10	—	3		3
—	146085		63718	59853	57204		58834		64512

* Missing Inter-combinations. Missing satellites.

TABLE III

The term values of Cd III

Term	Value	Term	Value	Term	Value
$4d^{10}\ {}^1S_0$	308463	$4d^9 5p\ {}^3F_4$	169422	$4d^9 6s\ {}^3D_3$	104033
$4d^9 5s\ {}^3D_3$	228000	,, $\ {}^3F_3$	172240	,, $\ {}^3D_2$	103545
,, $\ {}^3D_2$	226100	,, $\ {}^3F_2$	165699	,, $\ {}^3D_1$	98230
,, $\ {}^3D_1$	222234	,, $\ {}^3D_3$	165560	,, $\ {}^1D_2$	97864
,, $\ {}^1D_2$	219582	,, $\ {}^3D_2$	168024		
		,, $\ {}^3D_1$	160827		
		,, $\ {}^3P_2$	174641		
		,, $\ {}^3P_1$	169699		
		,, $\ {}^3P_0$	166341		
		,, $\ {}^1F_3$	162361		
		,, $\ {}^1D_2$	159980		
		,, $\ {}^1P_1$	162378		
$4d^9 5d\ {}^3G_5$	103342	$4d^9 5d\ {}^3D_2$	101650	$4d^9 5d\ {}^1G_4$	104996
,, $\ {}^3G_4$	103156	,, $\ {}^3D_1$	98304	,, $\ {}^1F_3$	88457
,, $\ {}^3G_3$	108462	,, $\ {}^3P_2$	109923	,, $\ {}^1D_2$	98789
,, $\ {}^3F_4$	98944	,, $\ {}^3P_1$	103863	,, $\ {}^1P_1$	95828
,, $\ {}^3F_3$	103045	,, $\ {}^3P_0$	101585	,, $\ {}^1S_0$	100475
,, $\ {}^3F_2$	97614	,, $\ {}^3S_1$	105485		
,, $\ {}^3D_3$	102365				

TABLE IV

The catalogue of the classified lines of doubly-ionized Cadmium

Plate II		Plate III					
Int.	No.	Int.	No.	—	—	—	Classification
—	—	0	1	1256.834	79565		$4d^9\ 5p\ {}^3D_2 - 4d^9 5d\ {}^1F_3$
—	—	½	1	61.538	79268		,, ,, $\ {}^3P_1 - b_0$
—	—	1	1	67 245	78911		,, ,, $\ {}^3F_4 - d_4$
—	—	0	0^+	68.838	78813		$4d^9\ 5p\ {}^3P_2 - 4d^9 5d\ {}^1P_1$
—	—	0^+	0^+	94·750	77235	42	,, ,, $\ {}^3F_2$ — ,, ,, $\ {}^1F_3$
0	0^+	0	2	1303·395	76782	IV?	,, ,, $\ {}^3P_2$ — ,, $6s\ {}^1D_2$
0	1	0	2	13.718	76120	IV?	,, ,, $\ {}^3P_2 - b_2$
—	—	0^+	0	26.421	75391		,, ,, $\ {}^1P_1 - a_0$
—	—	0	1^+	32.335	75053	IV?	,, ,, $\ {}^3D_3 - d_4$
0	0^+	0^+	0^+	53.164	73904		,, ,, $\ {}^1F_3 - 4d^9\ 5d\ {}^3F_3$
1	2	3	3	54.304	73839		,, ,, $\ {}^3D_1 - a_0$
0^+	0^+	0	0^+	56.389	73725		,, ,, $\ {}^3P_2 - b_1$
—	—	0	0^+	61.412	73453		,, ,, $\ {}^3F_3 - 4d^9\ 5d\ {}^1D_2$
3	4	5	5	83.618	72274		,, ,, $\ {}^3P_2$ — ,, ,, $\ {}^3D_3$
2	3	4	5	85.156	72194		,, ,, $\ {}^3D_2$ — ,, ,, $\ {}^1P_1$
—	—	1	1	91.807	71850		,, ,, $\ {}^1F_3 - d_4$
1	3	4	5	92.106	71834	IV?	,, ,, $\ {}^3P_1 - 4d^9\ 6s\ {}^1D_2$
4	4	5	5	96.779	71593		,, ,, $\ {}^3P_2$ — ,, $\ 5d\ {}^3F_2$
1^+	2^+	4	4	97.925	71535		,, ,, $\ {}^1D_2$ — ,, ,, $\ {}^1F_3$
—	—	1	1	99.101	71474		,, ,, $\ {}^3P_1$ — ,, $\ 6s\ {}^3D_1$
1^+	2^+	4	5	1400.696	71393	Gr.IV	,, ,, $\ {}^3P_1$ — ,, $\ 5d\ {}^3D_1$
1	3	3	5	06.564	71096	Gr.IV	,, ,, $\ {}^3P_2$ — ,, $\ 6s\ {}^3D_2$
3	3	5	5	16.250	70609		,, ,, ,, — ,, ,, $\ {}^3D_3$
0^+	1	1	1^+	16.627	70590		,, ,, $\ {}^3F_3$ — ,, $\ 5d\ {}^3D_2$
3	4	6	6^+	18.875	70478		,, ,, $\ {}^3F_4$ — ,, ,, $\ {}^3F_4$

TABLE IV (*contd.*)

Plate II		Plate III		—	—	—	Classification
Int.	No.	Int.	No.				
3	3	4	4⁻	20.248	70410		$5d^9 5p\ ^3D_2 - 4d^9 5d\ ^3F_2$
3	3	4	4	20.479	70399		,, ,, $^3D_1 - b_0$
0	0+	0+	2	25.311	70160		,, ,, $^3D_2 - 4d^9 6s\ ^1D_2$
3	4	5	5	31.154	69874		$4d^9 5p\ ^3F_3 -$,, $5d\ ^3D_3$
3	4	5	5	1431.154	69874		$4d^9 5p\ ^3F_2 - 4d^9 5d\ ^1P_1$
2	3	3	4	32 815	69793		,, ,, $^3D_2 -$,, $6s\ ^3D_1$
—	—	0	0+	34.350	69718		,, ,, $^3D_2 -$,, $5d\ ^3D_1$
—	—	0	1	38.861	69500		,, ,, ,, $- b_2$
2	3	4	5	44.580	69224		,, ,, $^3P_1 - 4d^9 5d\ ^1S_0$
1	2	2	3	45.195	69195		,, ,, $^3F_3 -$,, ,, $^3F_3$
4	5	5	5	46.025	69155		,, ,, $^3P_2 -$,, ,, $^3S_1$
5	5	6	5	47.492	69085	Gr. IV	,, ,, $^3F_3 -$,, ,, $^3G_4$
4	4	5	5	55.684	68696		,, ,, ,, $-$,, $6s\ ^3D_2$
2	2	3	3	66.132	68207		,, ,, ,, $-$,, ,, $^3D_3$
1	1	2	3	68.175	68112		,, ,, $^3P_0 -$,, ,, $^3D_1$
,,	,,	,,	,,	,,	,,		,, ,, $^3P_1 -$,, $5d\ ^3P_0$
4	4	4	5	68 760	68085		,, ,, $^3F_2 -$,, ,, $^3F_2$
3	3	4	4	1469.495	68051		,, ,, $^3P_1 -$,, ,, $^3D_2$
1	1	2	3	69.760	68038		,, ,, $^3P_0 -$,, ,, $^3D_1$
4	4	4	4	70.400	68009	G. & W.	,, $5s\ ^3D_3 -$,, $5p\ ^1D_2$
4	4	5	5	71.896	67942		,, $5p\ ^3D_3 -$,, $5d\ ^3F_2$
0	1	2	3	74.153	67835		,, ,, $^3F_2 -$,, $6s\ ^1D_2$
0	0+	1	2	77.225	67696		,, ,, $^3D_3 -$,, ,, ,,
1	1+	3	4	82.213	67467		,, ,, $^3F_2 -$,, ,, $^3D_1$
—	—	0	0+	83.770	67396		,, ,, ,, $-$,, $5d\ ^3D_1$
2	2	3	4	91 262	67058		,, ,, $^3F_4 -$,, ,, $^3D_3$
3	5	4	5	91.785	67034	Gr. IV?	,, ,, $^3D_3 - b_2$
3	4	4	5	1501.120	66617	Gr. IV	,, ,, ,, $- 4d^9$,, $^3F_4$
2	2	3	4	01.600	66594		,, ,, $^3F_4 - C_4$
3	4	4	5	02.680	66548		,, ,, $^1P_1 - 4d^9 5d\ ^1P_1$
3	4	4	5	06.590	66375		,, ,, $^3D_2 -$,, ,, $^3D_2$
,,	,,	,,	,,	,,	,,		,, ,, $^3F_4 -$,, ,, $^3F_3$
2	3	3	5	09.090	66265	IV?	,, ,, ,, $-$,, ,, $^3G_4$
4	4	5	5	10.980	66182		,, ,, $^3P_2 -$,, ,, $^3G_3$
2	2	3	3	11 640	66153		,, ,, $^3P_1 -$,, $6s\ ^3D_2$
5	5	6 double	6	12.630	66110	G. & W. Gr. IV	,, $5s\ ^3D_3 -$,, $5p\ ^1D_2$
4	4	5	4	13.100	66090		,, $5p\ ^3F_4 -$,, $5d\ ^3G_5$
—	—	1	1	18.921	65836		,, ,, $^3P_1 -$,, ,, $^3P_1$
—	—	0	0+	22.988	65660		,, ,, $^3D_2 -$,, ,, $^3D_3$
5	5	6	6	23.636	65636	G. & W.	,, $5s\ ^3D_3 -$,, $5p\ ^1F_3$
4	5	5	5	28.380	65429		,, $5p\ ^3P_0 - b_1$
5	5	4	4	29.300	65390		,, ,, $^3F_4 - 4d^9 6s\ ^3D_3$
4	5	5	5	32 090	65270	G. & W.	,, $5s\ ^3D_2 -$,, $5p\ ^3D$
2	3	4	5	38.440	65001		,, $5p\ ^3D_1 -$,, $5d\ ^1P_1$
—	—	1	1	41.427	64791		,, ,, $^3F_2 - b_1$
2	3	4	4	45.170	64718		,, ,, $^3P_2 - 4d^9 5d\ ^3P_2$
1	2	2	3	50.090	64512		,, ,, $^1P_1 -$,, $6s\ ^1D_2$
3	3	4	4	50.452	64497		,, ,, $^1F_3 -$,, ,, ,,
1	3	3	3	50.910	64478	IV?	,, ,, $^3D_2 -$,, ,, $^3D_2$
3	4	4	5	52.180	64426		,, ,, $^3F_4 -$,, $5d\ ^1G_4$
3	4	5	6	56.490	64247		,, ,, $^3P_2 - c_3$
1	1+	2	3	58.537	64163		,, $5p\ ^3D_2 - 4d^9 5d\ ^3P_1$
1	1	2	3	58.655	64158		,, ,, $^1D_2 -$,, ,, $^1P_1$
0+	1	2	1	60.311	64090		,, ,, $^3F_3 - e_2$
5	5	6	6	60.680	64075		,, ,, $^1P_1 - 4d^9 5d\ ^3D_1$
4	4	4	4	61.355	64047		,, ,, $^3F_2 -$,, ,, $^3D_2$

TABLE IV (*contd.*)

Plate II		Plate III		—	—	—	Classification
Int.	No.	Int	No.				
3	4	4	5	1566.028	63856		$4d^95p\ {}^1P_1-b_2$
—	—	0	0+	66.508	63836		,, ,, $^1F_3-$,,
—	—	0+	0	68 180	63768	(78)	,, ,, $^3F_3-4d^95d\ {}^3G_3$
5	4	6	6	68.988	63734	G. & W.	,, 5s $^3D_2-$,, 5p $^1F_3$
3	2	4	4	69 413	63718	,,	,, ,, ,, $-$,, ,, $^1P_1$
1	1	2	2	69.691	63707		,, 5p ,, $-d_2$
3	3	4	4	72 615	63588	Gr. IV	,, ,, $^1P_1-4d^95d\ {}^1D_2$
3	4	3	4	73.100	63569		,, ,, $^1F_3-$,, ,, ,,
—	—	1	1	82 052	63209		,, ,, $^3D_1-$,, ,, $^3F_2$
4	4	5	6	82.408	63195		,, ,, $^3D_3-$,, ,, $^3D_3$
—	—	1	1	93.892	62740	(32)	,, ,, $^3D_3-C_4$
—	—	0	0+	96.209	62648		,, ,, $^3F_2-4d^95d\ {}^3F_3$
3	3	4	4	97.598	62594		,, ,, $^3D_1-$,, 6s $^3D_1$
—	—	1	1?	99 092	62536		,, ,, $^3D_2-$,, 5d $^3S_1$
1	1+	2	2	99.444	62521		,, ,, $^3D_1-$,, ,, $^3D_1$
2	2	3	3	99.668	62513		,, ,, $^3D_3-$,, ,, $^3F_3$
6	5	6	5	1601.576	62439	G. & W.	,, 5s ,, $-$,, 5p $^3D_3$
1	1	2	2	02.500	62403		,, 5p ,, $-$,, 5d $^3G_4$
0	0+	2	2	03.245	62373		,, ,, $^1D_2-$,, ,, $^3F_2$
0+	1	2	3	04.891	62310		,, ,, $^3D_1-b_2$
—	—	1	1+	05.142	62300	G. & W.	,, 5s $^3D_3-4d^95p\ {}^3F_2$
5	5	6	6	06.646	62241	,,	,, ,, $^3D_1-$,, ,, $^1D_2$
1	2	3	4	08 957	62152		,, 5p $^3F_2-$,, 6s $^3D_2$
1	2	2	3	09.641	62126		,, ,, $^1D_2-$,, ,, $^1D_2$
—	—	0	0+	11.858	62040		,, ,, $^3D_1-$,, 5d ,,
1	2	3	4	12.507	62015		,, ,, $^3D_3-$,, 6s $^3D_2$
—	—	0	0+	15.465	61902		,, ,, $^1P_1-$,, 5d $^1S_0$
—	—	0+	0+?	16.822	61850		,, ,, $^3F_3-C_3$
0	1+	2	4	19 223	61758	IV?	,, ,, $^1D_2-4d^96s\ {}^3D_1$
0+	1+	2	4?	21.146	61685		,, ,, ,, $-$,, 5d $^3D_1$
3	3	4	5	25.305	61527		,, ,, $^3D_3-$,, 6s $^3D_3$
—	—	0	0+	26.922	61466		,, ,, $^1D_2-b_2$; $4d^95p\ {}^1P_1-b_1$
5	5	8	8	28.528	61405	G. & W.	,, 5s $^3D_1-4d^95p\ {}^3D_1$
—	—	1	1	29.128	61383		,, 5p $^3F_2-d_2$
—	—	1	1	33.990	61200		,, ,, $^1D_2-4d^95d\ {}^1D_2$
—	—	1	1	40.470	60958		,, ,, $^3F_4-$,, ,, $^3G_3$
—	—	0	1+	42.709	60875	IV?	,, ,, $^3D_2-C_2$
—	—	1	1	44.850	60796		,, ,, $^1P_1-4d^95d\ {}^3P_0$
0+	2	2	4	46.682	60728	IV?	,, ,, ,, $-$,, ,, $^3D_2$
—	—	0+	0	51.245	60560		,, ,, $^3D_3-$,, ,, $^1G_4$
5	5	6	6	51 872	60537	G. & W.	,, 5s $^3D_2-$,, 5p $^3D_3$
5	5	6	6	55 647	60399	,,	,, ,, ,, $-$,, ,, $^3F_2$
1	1	2	0+?	56.957	60352		,, 5p $^3D_1-$,, 5d $^1S_0$
—	—	0+	0?	60.666	60217		,, ,, $^3F_2-$,, ,, $^3S_1$
—	—	2	3	66.795	59995		,, ,, $^1F_3-$,, ,, $^3D_3$
—	—	1	1	67 484	59971	,,	,, 5s $^3D_3-$,, 5p $^3D_2$
0+	0	2	0	69 200	59909	II?	,, 5p $^3D_1-b_1$
—	—	1	1	70.206	59873		,, ,, $^3D_2-c_2$
4	4	5	5	70.748	59853	G. & W.	,, 5s $^3D_1-4d^95p\ {}^1P_1$
0	0+	1	1	73.037	59772		,, 5p $^3P_1-$,, 5d $^3F_2$
5	5	6	6	78.143	59595	G. & W.	,, 5s $^1D_2-$,, 5p $^1D_2$
—	—	1	1	78.908	59560		,, 5p $^3D_2-$,, 5d $^3G_3$
—	—	2	1	79.878	59528		,, ,, $^1F_3-c_4$
0	0+	1	2	85.846	59317		,, ,, $^1F_3-4d^95d\ {}^3F_2$
0	1	2	2+	88.022	59241		,, ,, $^3D_1-$,, ,, $^3P_0$
1	2	2	3	99.704	59834		,, ,, $^1P_1-$,, 6s $^3D_2$

TABLE IV (*contd.*)

Plate II		Plate III		—	—	—	Classification
Int.	No.	Int.	No.				
3	3	4	4	1702.038	58753	G & W.	$4d^95s\ ^1D_2 - 4d^95p\ ^3D_1$
5	5	10	9	07.156	58578	,,	,, ,, $^3D_3$ — ,, ,, $^3F_4$
—	—	1	0	08.056	58546		,, 5p $^3F_2 - C_2$
—	—	1	1	09.040	58512		,, ,, $^1P_1 - 4d^95d\ ^3P_1$
—	—	1	1	12.040	58410		,, ,, $^3D_3 - C_2$
—	—	1	1	21.273	58097		,, ,, $^3D_3 - 4d^95d\ ^3P_2$
		double					
5	5	8	8	21.898	58075	,,	,, 5s $^1D_2$ — ,, 5p $^3D_2$
1	2	2	3	22.936	58040		,, 5p $^1F_3 - d_2$
—	—	0	1	43.093	57360		,, ,, ,, — $4d^95d\ ^1G_4$
0	1	2	3	45.743	57282		,, ,, $^3D_1$ — ,, 6s $^3D_2$
—	—	1	1	47.074	57239		,, ,, $^3F_2$ — ,, 5d $^3G_3$
5	5	8	8	47.657	57210	,,	,, 5s $^1D_2$ — ,, 5p $^1F_3$
5	5	5	5	48.143	57204	,,	,, ,, ,, — ,, ,, $^1P_1$
	—	0	0+	56.069	56945		,, 5p ,, — ,, 5d $^3F_3$
5	5	8	8	68.818	56535	,,	,, 5s $^3D_3$ — ,, 5p $^3F_2$
5	5	8	8	73.043	56400	,,	,, ,, $^3D_2$ — ,, ,, $^3P_1$
—	—	0	0+	86.990	55960		,, 5p $^1D_2$ — ,, 6s $^3D_3$
5	5	6	6	89.208	55891	,,	,, 5s $^3D_1$ — ,, 5p $^3P_0$
—	—	1	0	92.751	55780		,, 5p $^3F_2$ — ,, 5d $^3P_2$
		double					
5	5	8	8	93.402	55760	,,	,, 5s $^3D_3$ — ,, 5p $^3F_3$
—	—	0	1+	97.286	55639		,, 5p ,, — ,, 5d $^3P_2$
—	—	1	1	1808.204	55303		,, ,, $^3F_2 - C_3$
—	—	1	1	43.038	54232	S?	,, ,, $^1P_1 - c_2$
6	6	8	8	44.670	54211	G & W.	,, 5s $^3D_1 - 4d^95p\ ^3D_2$
5	5	6	6	51.114	54022	,,	,, ,, $^1D_2$ — ,, ,, $^3D_3$
5	5	5	5	55.858	53883	,,	,, ,, ,, — ,, ,, $^3F_2$
6	6	6	6	56.698	53859	,,	,, ,, $^3D_2$ — ,, ,, $^3F_3$
6	6	10	10	74.113	53359	,,	,, ,, $^3D_3$ — ,, ,, $^3P_2$
4	4	5	-	1903.492	52535	,,	,, ,, $^3D_1$ — ,, ,, $^3P_1$
-	5	—	—	39.58	51557	,,	,, ,, $^1D_2$ — ,, ,, $^3D_2$
—	3	—	—	43.31	51459	,,	,, ,, $^3D_2$ — ,, ,, $^3P_2$
—	6	—	—	2004.73	49882	,,	,, ,, $^1D_2$ — ,, ,, $^3P_1$
—	1	—	—	2101.17	47592	,,	,, ,, $^3D_1$ — ,, ,, $^3P_2$
—	8	—	—	2112.31	47341	,,	,, ,, $^1D_2$ — ,, ,, $^3F_3$
—	4	—	—	2225.13	44941	,,	,, ,, ,, — ,, ,, $^3F_2$

are undoubtedly Cd III lines, some may be blends and one line, namely, 71096, is more likely to be a Cd IV than a Cd III line. Out of several plates taken during the investigation only two have been measured; intensities obtained from both the plates with and without inductance are given in the table. From these figures it is easy, in the light of the variation of intensities of the lines used by Gibbs and White, to infer the stage of ionisation of the respective lines The doubtful cases have been marked 'IV' with a sign of interrogation.

It seems necessary to mention four cases where lines appear by violating the selection rule; but as they can be explained away in the following manners they have not been included in the tables. There is a line '59873' for the combination $4d^{10}5s\ ^3D_1 - 4d^{10}5p\ ^3F_2$ exactly equal to the difference of the respective term-values. Its wave-length, 1670.206, is double the wave-length of the

oxygen line 835.10; but it should be mentioned that other members of this group of lines have not appeared in the 2nd order. A line appears in the place of the combination $4d^9 5p\ ^3P_0 - 4d^9 5d\ ^3P_2$. Its intensity is 'o+' and 'o' with and without inductance, so it can be a Cd II line. The combination $5p\ ^3P_1 - 5d\ ^3F_2$ seems to appear with intensity 'o+' and 'o+' with and without inductance; but on a very close examination of Plate III (only in this plate the line has appeared), its appearance without inductance is seen to be extremely doubtful. It may be then a Cd IV line. The line '73592' for the combination $5p\ ^3F_4 - 5d\ ^1P_1$ has been found and measured in both the Plates II and III with intensities 'o' and 'o+', and '1' and 'o+' with and without inductance. The author has also found a line '73597' in the zinc spectra which did neither fit into the analytical scheme for Zn II nor into that for Zn III and it could not be a Zn IV line on account of its behaviour with respect to inductance. Both these lines may be the same line and an impurity line.

In conclusion the author wishes to express his deep sense of gratitude to the late Prof. A. Fowler of the Imperial College, London, for suggesting the problem, to Prof. M. Siegbagn for permitting him to work in the Fysicum of the Upsala University, to Dr. D. M. Bose, Director of the Bose Research Institute, Calcutta, for permission to use the Library of the Institute, and to the Authority of Tata Iron & Steel Works, Ltd., for permission to continue the work in their Research Laboratory.

The New Control and Research Laboratory,
Tata Iron & Steel Works.

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PROCEEDINGS

OF THE

INDIAN ASSOCIATION FOR THE CULTIVATION OF SCIENCE

A scientific meeting of the Indian Association for the Cultivation of Science was held on 6th April, 1943 in the Association Hall. Sir U. N. Brahmachari, Kt., M.A., M.D., Ph.D., presided. The papers read are given in the following pages.

J. N. MUKHERJEE,
Honorary Secretary.

STANDARD STATE OF DESICCATION OF DRIED BLOOD PLASMA AND THE ADVANTAGES OF DESICCATION IN THE REGION OF MOLECULAR FLOW

By J. N. MUKHERJEE

AND

B. R. MAJUMDAR

(*Received for publication, May 22, 1943*)

INTRODUCTION

Dried blood plasma, used for transfusion purposes, is desiccated at comparatively low temperatures to prevent the denaturation of the plasma proteins. The stability of the products depends upon the amount of residual moisture and a standard method of its estimation should be followed. It appears also from a study of the literature that a standard state of 'dry' plasma has not been specified.

Flosdorf and Webster, in 1937, measured the residual moisture of dried blood plasma from the percentage losses in weights of the product when desiccated under different conditions. The results are given in Table I.

TABLE I

Percentage loss obtained under different conditions of desiccation

Time in hours	P_2O_5, pressure 100 microns	P_2O_5, pressure 1 atmosphere	50°C, pressure 100 microns
24	0.61	0.59	0
48	1.32	0.80	0.1
72	1.28	0.82	Increased in weight
98	1.31	0.82	" "

It will be seen from Table I that constant weight is attained in each case but the residual moisture content is different.

Greaves and Adair (1939) found the loss of moisture of a sample of blood plasma dried over P_2O_5 at a high vacuum (order not mentioned) at room temperature to be between 0.42 and 0.56%.

Blood plasma previously dried over silica gel at a pressure of 200 microns was desiccated over P_2O_5 at two different pressures and the results are given in the following table. In the experiments recorded in column 2 the desiccating vessel used was what is known as "drying pistol" (Gattermann 1937). A vacuum of very high order could be maintained in it. The other experiment (column 3) was carried out in a vacuum desiccator previously tested to be free from leaks.

The experiments were made at room temperature and no heat was supplied to make up for the loss due to evaporation.

TABLE II

Time in hours	% loss of moisture when desiccated over P_2O_5 at 0.1 micron	% loss of moisture when desiccated over P_2O_5 at 100 microns
24	1.82	0.23
48	2.26	0.41
72	2.35	0.52
90	2.35	—
92	—	0.62
96	2.35	—

It is evident from the above table that losses of moisture at the two different orders of vacuum are quite different and that for a pressure of 100 microns, the percentage loss does not attain a constant value.

The rate of evaporation at a pressure of the order of 100 microns is expected to be slower than that at the region of molecular flow which is reached at a pressure of 0.1 micron or less, *i.e.*, 10^{-4} m.m. Hg.

The general equation representing the flow of gas is given by

$$T=(ap+b)\ (1+c_1p)/(1+c_2p),$$

where T represents $Q/(p_1-p_2)$, the amount of gas exhausted per unit of time and p=the mean pressure, *i.e.*, $=(p_1+p_2)/2$ where p_1 and p_2 are the pressures (Loeb, 1929) at the two extremeties of the evacuated vessel, and a, b, c_1 and c_2 are constants. In the region of molecular flow the equation reduces to $T=b$ and collisons between molecules are negligible in comparison with those between the molecules and the walls of the vessel. If we consider that P_2O_5 acts as a 'perfect sink' for molecules of water, then a steady state must be attained when no further loss in weight of the substance can take place and the product thus obtained may be taken to represent the standard state of desiccation (Table II, column 2). The dried product was found to be soluble in water but no further examination of the product was made. It is also apparent that quicker desiccation has been achieved by using vacuum which falls in the region of molecular flow.

Our thanks are due to Dr. J. B. Grant, Director of All-India Institute of Hygiene and Public Health, for the sample of dried plasma which was sent for the determination of its residual moisture.

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2

EFFECT OF SAND ON THE VISCOSITY, YIELD VALUE AND THIXOTROPIC GELATION OF MUD SUSPENSIONS

By J. N. MUKHERJEE

AND

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(*Received for publication, May 22, 1943*)

Mud is now-a-days used as the lubricationg fluid for the rotary drilling of oil-wells. Properties of mud and clay suspensions are of interest to several other industries, *e.g.*, ceramics. This work was undertaken to investigate the probable causes of stuck drill pipes in oil-wells. The effect of the sand concentration in modifying the viscous properties and thixotropy of drilling mud has been studied.

EXPERIMENTAL

A. *Preparation of mud suspension.*—Powai clay from Digboi was used. A very stable suspension could be prepared from this sample by simply suspending it in water and a fairly thick suspension having thixotropic property had a weight of 78 lbs. per cubic ft. and a pH of 4.85 (determined by glass electrode). This suspension will be called PC-L1 henceforth.

B. *Sampling of sand.*—The following two grades of sand having different grain sizes were collected by sieving a sample of ordinary sand through standard sieves :

Grade I.—Passing through 48-mesh sieve but retained by 100-mesh sieve.

Grade II.—Passing through 100-mesh sieve.

These two grades of sand were incorporated into mud suspension PC-L1 to increase the sand concentration in it.

C. *Appparatus used and experimental detail.*—Stormer Viscometer (Bark, 1931) was found to be very suitable for measuring viscosities, relative yield values and the rate of thixotropic gelation. Viscosities were determined as follows: Weights required for the movement of the inner cylinder of the viscometer at 600 r.p.m. were noted and the corresponding viscosities calculated from the weight-viscosity curve of standard liquids.

The thixotropic gel strength of the mud suspension was followed by measuring the speed of the inner cylinder of the viscometer after different intervals of rest given to a freshly formed suspension.

The water filtration tests were carried out in a Jones-Babson tester. Such measurements reveal the wall-building properties of mud suspensions and this is an essential factor in characterising oil-well drilling mud.

RESULTS AND DISCUSSION

The results of chemical (Wright, 1934a) and mechanical (Wright, 1943b) analyses of the original sample are given below:

TABLE 1

Chemical Analysis			Mechanical Analysis		
Moisture	...	4.33%	Clay	...	29.38%
Loss on ignition.	...	19 58%	Silt	...	15.32%
Silica	...	50.49%	Sand	...	24.99%
Fe_2O_3	...	4.13%	Loss on solution	...	3.44%
Al_2O_3	...	19.58%			
CaO	...	1.31%			
MgO	...	0.55%			

Viscosities of mud suspension containing varying amounts of sand are given in Table 2.

TABLE 2

Sample	Grade I sand	Grade II sand
PC–L1	30.0 c.p.	30. 0 c.p.
PC–L1+1% sand	33.5 ,,	34.50 ,,
PC–L1+2% ,,	34.0 ,,	34.50 ,,
PC–L1+3% ,,	32.0 ,,	32.25 ,,
PC–L1+4% ,,	30.0 ,,	34.50 ,,
PC–L1+5% ,,	31.0 ,,	45.00 ,,

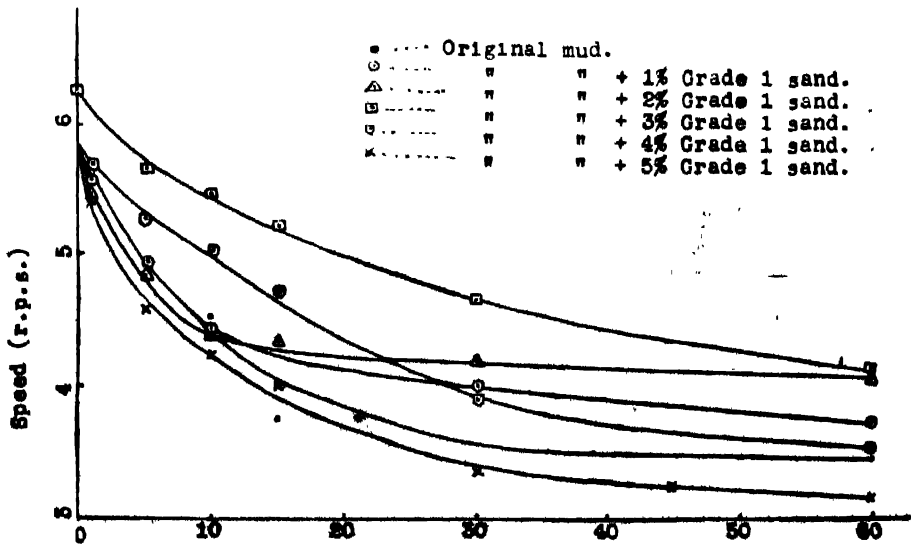

FIG. 1

With Grade I sand, there is no marked variation in the viscosity, but with Grade II sand, the viscosity of the sample whose sand concentration has been increased by 5%, is much higher than that of the other samples.

From the curves shown in Figs. 1 and 2, it appears that the thixotropic gel strength at first decreases with increase of sand concentration and above 3% of additional sand concentration, it again increases. The relation holds good for Grade I and Grade II sands. The relative yield values of the mud suspension as indicated by the same curves in Figs. 1 and 2 also vary with sand concentration.

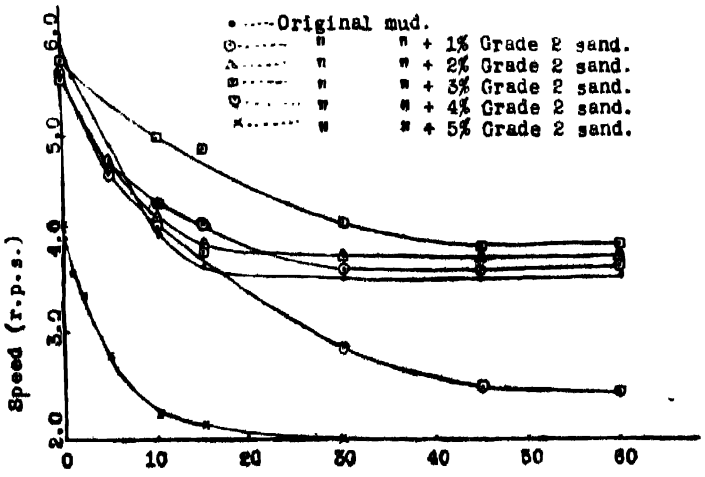

FIG. 2

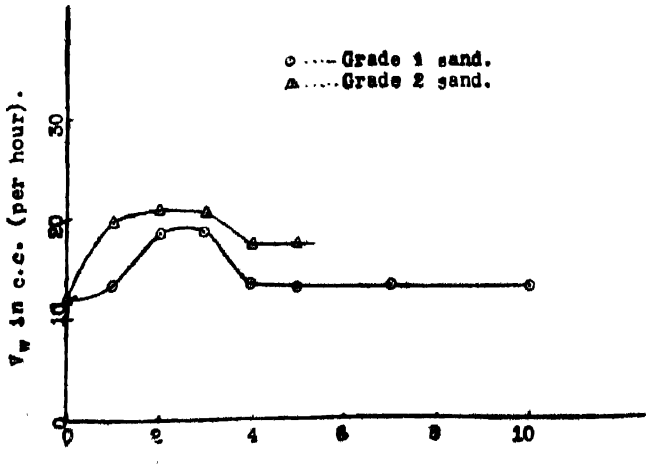

FIG. 3

Water filtration tests show that V_w (cumulative volume of water in c.c.) after 1 hour at first increases and above 3% additional sand concentration it decreases (Fig. 3). From the above results it may be concluded that there exists a critical sand concentration for this mud suspension, above which thixo-

tropic property, the relative yield value, V_r of the mud suspension are modified. This observation throws some light on probable causes of sticking of drill pipe.

The relative permeability of sheaths formed from samples containing Grade II sand is higher than that formed from sample containing Grade I sand.

The moisture content of sheaths formed was also determined. The results are shown below:

TABLE 3

	Sample	Grade I sand		Grade II sand	
		Total solid %	Moisture %	Total solid %	Moisture %
1	PC–L_1	58.61	41.39	58.61	41.39
2	PC–L_1 + 1% Sand	90.42	39.58	59.58	40.02
3	PC–L_1 + 2% ,,	—	—	60.47	39.53
4	PC–L_1 + 3% ,,	60.71	39.29	61.11	38.89
5	PC–L_1 + 4% ,,	61.41	38.59	61.81	38.18
6	PC–L_1 + 5% ,,	61.50	38.50	62.19	37.81
7	PC–L_1 + 7% ,,	62.10	37.90	—	—
10	PC–L_1 + 10% ,,	63.59	37.41	—	—

The moisture content at sticky point (Wright, 1934c) of original mud = 28.52%. Table 3 shows that the moisture content of the sheaths formed from the mud suspension containing varying amounts of sand is higher than this value. Actually, all the sheaths were sticky.

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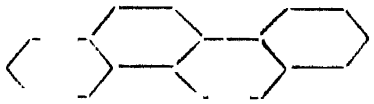
ON THE FLUORESCENCE OF ANTHRACENE IN PRESENCE OF NAPHTHACENE

By S. C. GANGULY

It is known that pure naphthacene crystal  fluoresces very feebly, and in dilute solid solution of anthracene  , the crystal fluoresces with its characteristic yellow-green light, but the blue fluorescence of anthracene is quenched. This phenomenon is represented as follows: In dilute solid solution the anthracene molecules easily absorb light energy and releases an 'excition' which excition causes naphthacene to fluoresce. Not only in anthracene, but in chrysene  also we find solid napthacene to fluoresce, only there is little shifting of the fluorescence bands, the shifting depending on the substance with which it is mixed. In consideration of above facts, study of fluorescence spectra in alcoholic solution of anthracene, naphthacene and the mixture of the above two, is interesting. In alcoholic solution anthracene has got four fluorescence bands (excited by 3650, 4046 of Hg arc), naphtacene has three fluorescence bands on the redside of the fluorescence bands of anthracene and the mixture has both the fluorescence of anthracene and naphthacene. Three solutions are prepared, one of pure anthracene, the other of pure naphthacene and the third is the mixture of the above two. The number of gram-molecules per c.c. of anthracene and of naphthacene in the mixture are identical with those for pure substances taken separately. Exposures are given for the same time and under identical conditions. It is observed that the intensity of fluorescence bands of anthracene is not changed at all due to the presence of naphthacene. The intensity of fluorescence of naphthacene also due to the presence of anthracene is not increased. Absorption spectra of the above three solutions confirm the results.

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4

MAGNETIC STUDIES ON PERMANGANATES

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The principal susceptibilities of $KMnO_4$ and $Ba(MnO_4)_2$ crystals have been measured by the method of Krishnan and his collaborators. The anisotropy in in case of $KMnO_4$ is .07 and the effective magnetic moment=0.5 Bohr magnetons. The anisotropy is correlated with the known fine structure of the crystal in the following manner.

Krishnan and the present writer have shown that anisotropy of paramagnetic crystals arises from certain paramagnetic units. Those units are constituted as follows: each paramagnetic ion in the crystal is under the influence of the electric field of its neighbours. The magnitude and assymmetry of this field is determined by the positions of the atoms immediately surrounding the paramagnetic ion. If this field is assymmetric the crystal will exhibit magnetic anisotropy. In general there will be more than one such group in the unit cell of the crystal. So the crystal anisotropy is determined by the anisotropy of these units and their orientations relative to one another.

In ($KMnO_4$) crystal (MnO_4) group is the paramagnetic unit. From the fine structure study of $KMnO_4$ crystals by Mooney it appears that in MnO_4 group the four oxygen atoms are disposed more or less symmetrically about the manganese atom, being situated at the corners of a tetrahedron with manganese at the centre. The manganese to oxygen distances are: two oxygen atoms at 1·58 Å, one oxygen at 1.68 Å and one at 1 52 Å. So the tetrahedron of oxygens is not a regular one and the crystalline electric field will deviate from cubic symmetry; the result is that the MnO_4 group will exhibit anisotropy.

On seeking the explanation of the feeble paramagnetism by Pauling's method of directed electron pair bonds one finds that in these compounds d^3sp^3 bonds should result which make them diamagnetic but measurements show that they are feebly paramagnetic. This feeble paramagnetism can be explained by Van Vleck's electric field theory as follows.

The electric field surrounding the paramagnetic ion in this case is taken so strong that Russell Saunder's coupling between the different electrons in the ions is broken. According to Van Vleck the Stark pattern of electron consists of two levels when the symmetry of the field is cubic. Since in $KMnO_4$ crystals the crystalline electrical field deviates from cubic symmetry, one of them will further split into two and the other into three levels. This splitting exceeds 3×10^4 cm^{-1} in order to uncouple the individual 's'. According to Gorter the group of two levels will be lowest as the arrangement about Mn in MnO_4 is tetrahedral. The deepest state will then be obtained by assigning the four

electrons responsible for paramagnetism in these two levels. All the electrons will then double up and there will be no spin free because of Pauli's exclusion principle and hence spin will contribute nothing to paramagnetism. So the only contribution to paramagnetism will be from the high frequency part of the orbital moment. Howard has shown that in case of $K_3Fe(CN)_6$ the high frequency orbital contribution to paramagnetism is about 0.5 Bohr magneton. In case of Mn^{+++} complex it is 0.5 Bohr magneton, which agrees satisfactorily with our experimental results for the permanganates.

It is interesting to note that the two lowermost levels are equally populated and hence anisotropy should be small in agreement with experimental facts.

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